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Citation: The Journal of Chemical Physics **83**, 3481 (1985); doi: 10.1063/1.449152 View online: http://dx.doi.org/10.1063/1.449152 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/83/7?ver=pdfcov Published by the AIP Publishing

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Coaxial measurement of the translational energy distribution of CS produced in the laser photolysis of CS_2 at 193 nm

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(Received 25 March 1985; accepted 13 June 1985)

Carbon disulfide (CS₂) photolysis was investigated in the gas phase using an argon fluoride (ArF) laser at 193 nm. The coaxial time-of-flight (TOF) distributions of CS radicals produced in the photolysis have been measured. Photochemical fragments have been observed with translational energies below 3 kcal/mol. The vibrational distribution of the CS fragments was also probed by laser induced fluorescence (LIF), and these measurements confirm that significant amounts of CS radicals are produced in vibrational levels greater than v'' = 6. From a computer simulation of the experimental LIF data, a vibrational distribution was also obtained. Vibrational levels up to v'' = 12 were found to be populated in a bimodal distribution, which peaks at v'' = 4, and extends to v'' = 12. There was a significant amount of rotational excitation of nascent CS produced in high vibrational levels of the ground state. The disjoint translational energy and CS vibrational energy distributions can be used to obtain an estimate of the S(³P) to S(¹D) ratio of 0.66.

I. INTRODUCTION

The photolysis of carbon disulfide (CS_2) in the 180 to 210 nm region has been investigated using various techniques, but its photochemistry is still not completely understood. Earlier photochemical studies employed atomic absorption photometry,¹ resonance fluorescence,² flash photolysis³⁻⁶, and dissociative excitation.⁷ The advent of rare gas-halogen excimer lasers, and tunable dye lasers has opened the way for even more detailed studies of the photodissociation dynamics of CS_2 . These studies include the two-photon dissociation of CS₂ with a KrF laser,⁸ atomic resonance fluorescence detection of S atoms produced from the ArF laser photolysis,⁹ isotope separation of carbon and sulfur atoms by an ArF laser,¹⁰ measurements of electronically excited fragments from the photolysis of CS₂ by an ArF laser,¹¹ laser induced fluoresence, 12,13 and velocity measurements of the CS fragments.¹³ The reader is referred to the excellent reviews by Filseth¹⁴ and Ashfold et al.¹⁵ on the photochemistry of CS₂ in the VUV region.

CS₂ absorbs strongly in the 180–210 nm region, with an absorption cross section at 193 nm of about 2×10^{-16} cm². The transition in this region is from a linear $...(\pi_g)^{4-1}\Sigma_g^{+}$ ground state to the $...(\pi_g)^3(\pi_u^*)^{1-1}\Sigma_u^{+}$ excited state. The ${}^{1}\Sigma_u^{+}$ excited state correlates to a bent ${}^{1}B_2$ state with C_{2v} symmetry. It has been shown that in the excitation the CS bond lengthens from 1.55 to 1.66 Å, and the bond angle changes from 180 to 153 deg.^{16,17} The absorption spectrum shows that both the symmetric stretching and bending modes are excited in the 193 nm transition.^{16,17}

The geometrical changes that the CS_2 molecule undergoes in connection with light absorption can have a large effect on the dynamics of the dissociation process. The energetics of CS_2 photolysis at 193 nm leads to two possible photodissociation channels¹⁸:

$$CS_{2}(X^{T} \Sigma_{g}) + h\nu \rightarrow CS(X^{T} \Sigma) + S({}^{3}P),$$

$$\Delta H = 45.0 \text{ kcal/mol}, \qquad (1)$$

$$CS_{2}(X^{T} \Sigma_{g}) + h\nu \rightarrow CS(X^{T} \Sigma) + S({}^{1}D),$$

$$\Delta H = 18.6 \text{ kcal/mol}, \qquad (2)$$

where the value of hv is taken at the region of maximum overlap of the laser emission and the CS₂ absorption.¹⁶

A controversy has arisen with respect to the branching ratio between the channels that produce $S({}^{1}D)$ and $S({}^{3}P)$, and the vibrational distribution of the CS product. It has been suggested that the formation of $S({}^{3}P)^{3,6,9}$ is the dominant channel, while Yang *et al.*¹³ suggest that production of $S({}^{1}D)$ is dominant, and the CS fragments are mostly produced in vibrational levels lower than v'' = 6. In particular, Refs. 3 and 6 were indirect measurements that ascertained that the principal photolysis channel in the ultraviolet dissociation of CS_2 leads to the formation of triplet sulfur, i.e., $S({}^{3}P)$.

The controversy was heightened by the work of Addison et al.,⁹ who employed a direct method of measuring the relative amounts of $S(^{1}D)$ to $S(^{3}P)$. Briefly, Addison et al.⁹ used time-resolved resonance fluorescence to observe $S(^{1}D)$. Carbon disulfide in a static cell was photolyzed at 193 nm using an argon fluoride laser. Nascent sulfur atoms in both electronic states were excited by an atomic resonance lamp. The fluorescence of both $S(^{1}D)$ and $S(^{3}P)$ was monitored at 166.7 and 180.7 nm, respectively, by a solarblind photomultiplier. The amount of $S(^{1}D)$ formed was measured by observing the change in the $S(^{3}P)$ concentration before and after the addition of nitrogen, which quenches $S(^{1}D)$ efficiently. From their observations they concluded that an upper limit to the $S(^{1}D)$ yield was $15\% \pm 6\%$. Though Addison et al.⁹ experiment is in principle more sensitive to the production of the nascent atomic products, in practice their results may be plagued by certain experimental difficulties. Specifically, their published decay curves do not indicate how the $S(^{1}D)$ fluorescence decay signal varies in the first $20 \mu s$. From their quoted experimental conditions, one calculates that approximately 20% of the CS_2 is dissociated per shot. Because they

0021-9606/85/193481-10\$02.10

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J. Chem. Phys. 83 (7), 1 October 1985



FIG. 1. Schematic of molecular beam photolysis apparatus for TOF measurement with coaxial geometry.

did not flow the reactant gases, a large percentage of the original CS_2 will be destroyed during their sampling time of 10–20 shots. Furthermore, Wollrab *et al.*¹⁹ has shown that the lifetime of CS radicals is of the order of 30 min. The presence of these radicals can cause further complications in Addison *et al.*⁹ experiment.

Yang et al.¹³ argue that very rapid quenching of $S({}^{1}D)$ by CS_{2} is the reason that the other experiments detected only $S({}^{3}P)$. On the other hand, since Yang et al.¹³ measured the TOF of the CS fragments using a mass spectrometer detector which is perpendicular to the axis of the molecular beam, fragments with very low velocities would escape detection in their apparatus. Following their analysis, the presence of such low velocity fragments implies an even higher $S({}^{1}D)/S({}^{3}P)$ ratio, which makes the discrepancy between their results¹³ and the others^{3,6,9} even worse. In light of this, it was felt that newer studies on the photolysis of CS_{2} at 193 nm were warranted.

In this paper experiments will be described in which low velocity CS fragments were measured with a mass selective TOF detector oriented along the molecular beam axis to measure the slow velocity fragments. In order to confirm the interpretation of the TOF results, a series of LIF experiments were also performed to probe the upper vibrational levels of nascent ground state CS radicals.

II. EXPERIMENTAL

A. Time-of-flight experiments

A schematic diagram of the TOF apparatus is shown in Fig. 1. A supersonic molecular beam was formed with a Laser Technics pulsed valve source, equipped with a 0.5 mm nozzle. The molecular beam was crossed 2 cm downstream by an unfocused ArF laser beam produced by a Lambda Physik EMG 101 excimer laser. The ArF laser intensity in the TOF work was about $30-40 \text{ mJ/cm}^2$ per pulse, and the laser beam dimensions at the interaction region were 7×15 mm. The pressure behind the nozzle was 50 Torr of CS₂. The CS₂ was obtained from Fisher Scientific and was outgassed by a number of freeze-thaw cycles.

The pulsed beam and the fragments were passed through a skimmer, through the buffer chamber, and into the ionizer of an Extranuclear quadrupole mass spectrometer, which was in a separate chamber. The ionizer was 13.4 cm downstream from the interaction region where the laser and the molecular beam crossed each other. The first chamber was equipped with two 39 cm stainless steel arms which contained baffles to aperture the ArF beam to 7×15 mm and reduce the scattered light for the LIF experiments. The first chamber was Teflon coated, and the baffles and arms were coated with Aerodag-G (Acheson Colloids). Both the first chamber and the buffer chamber were each pumped by a liquid nitrogen trapped six inch diffusion pump. The mass spectrometer chamber was pumped by an ion pump and a titanium getter pump. With this arrangement pressures of 5×10^{-8} Torr could be obtained in the mass spectrometer chamber with the beam on. Even so, there was still considerable background signal at both the CS⁺ and S⁺ mass peaks from the CS_2 in the beam which had undergone dissociative ionization. To overcome this, the electron energy was lowered to 15 eV to reduce the amount of dissociative ionization, and the molecular beam was pulsed at twice the rate of the laser beam. The ions at the detector were then counted positively in a multichannel analyzer, when both the molecular beam and the laser were on, and negatively when only the molecular beam was on.

A typical TOF spectrum of CS^+ is shown in Fig. 2. This spectrum exhibits a signal to noise ratio of about 5, which was obtained after 15 000 laser shots. The center-of-mass beam velocity was determined by measuring the decrease in the CS_2^+ parent peak as a result of the laser photolysis. The "drift time" for the ions inside the quadrupole was determined by sharply pulsing the extractor electrode and then



FIG. 2. A typical TOF spectrum of CS fragments taken with the coaxial geometry.

measuring the time it took for these ions to reach the electron multiplier.

B. Laser-induced-fluorescence experiments

The experimental arrangement shown in Fig. 3 was used for the LIF measurements. A flashlamp pumped dye laser (Candela LFDL-1) was used in the first LIF experiments. It has a pulsewidth of about $1.5 \,\mu s$ and a bandwidth of 0.1 nm. The laser output was doubled by a KDP crystal and the doubled beam was softly focused into the reaction cell. In these experiments the fluence of the ArF laser was at most 1-3 mJ/cm² per pulse. The laser beams were counterpropagating with respect to each other, with the dye laser beam completely embedded in the excimer beam. A photomultiplier tube (EMI 9789QB) was mounted perpendicular to both beams. The fluorescence was passed through a bandpass filter with a maximum transmission at 254 nm and a full width half-maximum bandpass of 23 nm. The filter blocked out the scattered dye laser and passed the emission from vibrational levels in the upper state of the laser excited CS, to levels in the ground state that occur at shorter wavelengths. The delay between the excimer laser and the dye laser was fixed at 2 μ s. Both lasers were pulsed synchronously at 4–6 Hz. Special care was taken so that the dye laser beam stayed on axis with the excimer beam as the angle tuned doubler was adjusted. Rhodamine 590 (Exciton) was used in the dye laser, which was scanned between 580 and 620 nm.

In all of the LIF experiments, the CS_2 was flowed through the system at a pressure of 10 mTorr or less. The pressure was monitored using a capacitance manometer (MKS 22 AHS Baratron, 0–10 Torr). The gas mixture must be flowed, so that production of CS from the photolysis of secondary products does not interfere with the measurements, and because CS radicals in the ground state react very slowly and might persist in the cell in between laser shots.¹⁹



FIG. 3. Schematic diagram of the LIF experimental apparatus.

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The fluorescence signal, collected at the PMT, was sent to a preamplifier and then to a photon counter (PRA 1770). The analog output from the counter, proportional to the number of counts registered in a fixed time period, was displayed on a stripchart recorder.

Although the tuning range is large, the bandwidth and power of the Candela flashlamp pumped dye laser are limited. Thus a Nd-YAG pumped dye laser (Molectron MY34, DL-18) was also used to characterize the distribution of CS nascent in the upper vibrational levels of the ground state. This dye laser has a bandwidth of 0.01 nm. Using Rhodamine 6G, Kiton Red, Rhodamine B (Exciton), and a WEX doubling unit (Quanta-Ray), a tuning range of 285-310 nm was obtained. The delay between the dye laser and excimer laser was varied between 200 ns and 20 μ s. At the shorter delays the CS₂ pressure had to be held especially low to limit interference from the prompt emission from CS2.¹² Both lasers were pulsed at 10 Hz. Again the CS₂ ws flowed, and the CS₂ pressure was kept at 1 mTorr. In some experiments, where rotationally relaxed vibrational distributions were measured, 100 to 1 mixtures of argon and CS₂ were used at total pressures of about 100 mTorr. The argon rotationally cools the CS so that the vibrational bands can be easily identified and measured. A boxcar analyzer was used to measure the photomultiplier current induced by the fluorescence.

III. RESULTS

A. Time-of-flight experiments

All of the measured TOF distributions of CS were converted to translational energy distributions using the experimentally determined beam velocities of the neutral CS2 molecule and the CS⁺ ion. The translational energy distributions obtained from both the coaxial and perpendicular detector orientations are shown in Fig. 4, along with those that were obtained from the perpendicular scattering geometry for the TOF distributions measured by Yang et al.¹³ We did only one experiment using the latter detection geometry, in order to demonstrate that Yang et al. results could be reproduced in our apparatus and provide a direct and quantitative cross-calibration between their work and ours. Figure 4 shows that the results of the earlier study can be reproduced in the region between 10 and 39 kcal/mol. Below 10 kcal/mol, both studies show that the results obtained using the perpendicular arrangement curve over, although they do so at different translational energies. Besides geometric effects, this is the type of behavior one might expect if the backing pressure behind the nozzles were different in the two experiments. Yang et al. do not report what backing pressure they used in their system.¹³

The results of Ref. 13 have been normalized to our results by matching the curves at the highest translational energies. A better agreement in the low energy range between the results of Ref. 13 and the present results could be achieved by normalizing each of the results with respect to each other at 8.4 kcal/mol. This, however, would give rise to a greater overall discrepancy in the other energy regions. It is in the higher energy regime, above 15 kcal/mol, that the perpendicular arrangement has the highest resolution and signal-to-noise ratio. It is also in this region that the differ-



FIG. 4. Translational energy distribution of CS fragments from the photolysis of CS₂ at 193 nm. This figure was obtained by inversion of the TOF spectrum. A comparison is shown of the results of coaxial and perpendicular detection configurations. (**•**) From coaxial detection averaged over five measurements: (O) from Yang *et al.* (Ref. 13); and (\triangle) one measurement at right angles in this work.

ences due to different pressures behind the beam nozzles will be the smallest. Therefore, we have chosen to normalize our results to those of Yang *et al.* at high translational energy. One would expect that the results should certainly agree in this region. With this renormalization there still is a discrepancy between the results of the perpendicular and coaxial detection geometries, due to the higher sensitivity of the latter geometry for detection of nascent fragments with low translational energies.

A break in the translational distribution at about 19 kcal/mol, described by Yang *et al.*, ¹³ is more clearly seen in the perpendicular geometry because of its higher resolution in the upper energy range. This high energy break has been ascribed by them to the cut off of the $S(^{1}D)$ channel in the photodissociation process. As mentioned in Ref. 13, strong evidence for this interpretation is the fact that the break occurs at the threshold energy for the production of $S(^{1}D)$. The analysis of the CS₂ spectrum suggests that in the state excited at 193 nm, some singlet-triplet mixing occurs.¹³ Recently this has been confirmed by another analysis of the CS₂ absorption spectrum around 200 nm obtained in a pulsed molecular beam.¹⁶

Energetically this break must correspond to the cutoff in the production of $S({}^{1}D)$. However, if one only has the TOF spectrum, it is not clear how to separate the part of the distribution below this energy that is associated with the production of $S({}^{3}P)$ from the part due to $S({}^{1}D)$. Yang *et al.*¹³ set a lower bound to the $S({}^{3}P)/S({}^{1}D)$ ratio by assigning all of those molecules with translational energies higher than the break to $S({}^{3}P)$, and all those with translational energies lower than the breakpoint to $S({}^{1}D)$. This procedure leads to a lower bound for the $S({}^{3}P)/S({}^{1}D)$ ratio of 0.18 from our measurements as compared to the Yang *et al.* value of 0.25.¹³ This is still unsatisfactory since it gives a very loose lower bound and is in conflict with the results of Refs. 3, 6, and 9. Such a

u V	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	257.7 (0.8462)	266.5 (0.1364)	275.7 (0.0159)	285.5 (0.0014)										
1	251.0 (0.1428)	259.3 (0.5620)	268.1 (0.2396)	277.3 (0.0484)	287.1 (0.0064)									
2	244.6 (0.0106)	252.4 (0.2629)	260.7 (0.3163)	269.5 (0.2956)	278.7 (0.0943)	288.6 (0.0175)								
3		246.1 (0.0364)	254.0 (0.3408)	262.3 (0.1339)	271.1 (0.2981)	280.4 (0.1458)	290.2 (0.0371)	300.6 (0.0066)						
4		240.3 (0.0022)	247.8 (0.0793)	255.7 (0.3629)	264.0 (0.0291)	272.8 (0.2519)	282.1 (0.1909)	291.9 (0.0659)	302.4 (0.0149)					
5			241.9 (0.0078)	249.5 (0.1358)	257.4 (0.3275)		274.6 ^b (0.1739)	283.8 (0.2169)	293.7 (0.1017)	304.2 (0.0292)				
6				243.7 (0.0205)	251* (0.1959)	259* (0.2468)	268* (0.0282)	276.4 (0.0894)	285.8 (0.2137)	295.6 (0.1398)	306.1 (0.0509)			
7					245.5 (0.0440)	253.1 (0.2442)	261* (0.1463)	269ª (0.0815)	278.4 (0.0253)	287.7 (0.1790)	297.6 (0.1682)	308.1 (0.0794)		
8					240.2 ^b (0.0045)	247.4 ⁶ (0.0799)	252 ^a (0.2641)	263 ^a (0.0576)	271.5 (0.1252)		289.8 (0.1212)	299.8 (0.1797)	310.3 (0.1115)	321.4 (0.0422)
9						242.1 (0.0123)	249.4 ^b (0.1258)	257.1 (0.2445)	265.2 (0.0070)	273.6 (0.1344)		. ,	302.0 (0.1660)	312.5 (0.1406)
10							244.1 ^b (0.0281)		. ,					305.3° (0.1276)

TABLE I. Transition wavelengths and Frank-Condon factors for $CS(A^{1}\Pi - X^{1}\Sigma^{+})Q$ -branch bandheads (from Ref. 20). Wavelengths given in nm.

*Estimated transition wavelengths not reported in Ref. 20.

^b R-branchead only (Ref. 21).

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^c This assignment was originally reported as 31 757.6 cm⁻¹ in Ref. 20; the correct value should be 32 757.6 cm⁻¹, and the correct transition wavelength is reported here.

lower bound is not a sufficient criteria for concluding that $S(^{1}D)$ is the major product of the photolysis.

B. Laser induced fluorescence experiments

The LIF spectra obtained in Refs. 12 and 13 are also not sufficient to show that the CS fragments only occur in vibrational levels lower than v'' = 6. The fact that no vibrational levels were identified above v'' = 6 is mostly the result of poor Franck-Condon factors for transitions connecting higher vibrational levels in the $\Delta v'' = 0$ and -1 sequences of the $A^{1}\Pi \rightarrow X^{1}\Sigma^{+}$ system. This can be seen in Table I, which lists the Franck-Condon factors and transition wavelengths. From Crawford and Shurcliff's measurements, the Franck-Condon parabola is quite wide as opposed to some other molecules, e.g., CN.^{21,22} Starting from high vibrational levels of the ground state of the CS the $\Delta v = -2$ and -3sequences have favorable Franck-Condon factors. From Bergeman and Cossart,²⁰ and as seen in Table I, one should be able to excite one or more transitions from levels between 5 and 13 in the wavelength region 280-315 nm. Indeed, close inspection of the LIF spectra of Refs. 12 and 13 show hints of other sequences, originating from higher ground state vibrational levels.

Previous CS₂ photolysis experiments with LIF detection, used ArF lasers that had energies of between 10 and 30 mJ per pulse. Recently, it has been shown that at such high energies there is a sequential two-photon absorption process in CS_2 at 193 nm.¹¹ The first photon is absorbed by the CS_2 , which then predissociates. A second photon is then absorbed by ground state CS radicals produced as a result of the first absorption process. The fact of these radicals from the absorption of a second 193 nm photon is determined by two possible channels, depending on the vibrational excitation of ground state CS. Nascent CS in vibrational levels lower than v'' = 5 will absorb a second 193 nm photon and make a transition to the CS(A') state. Since the lifetime of the A' state is 15 ns, the radicals can fluoresce or relax to upper vibrational levels of X state CS. In fact the redistribution process will populate vibrational levels between v'' = 10-30. Nascent CS in vibrational levels higher than v'' = 5 will be depleted by photodissociation to atoms. Such effects can also distort the TOF distribution. However the low signal to noise ratio in those experiments requires that one use a system with high fluence. Theoretically such a distortion could be resolved as extra peaks in the TOF distributions, but this would require a higher resolution than was available. LIF experiments, especially using the Nd-YAG pumped dye laser system, have a much higher sensitivity. Therefore, the excimer laser power was kept very low in the LIF experiments. Plots of LIF signals vs excimer laser power were linear, down to ArF laser fluences of less than $100 \,\mu$ J/pulse. In addition, we detected no CS in vibrational levels higher than 12, the thermochemical limit. If the sequential absorption redistribution mechanism was important at the lower ArF laser intensities that were used, then one would expect to see population in such higher vibrational levels.

Figure 5 shows the LIF spectrum obtained when the frequency-doubled flashlamp-pumped dye laser is scanned across the 290–305 nm region. Except for the lower ArF



FIG. 5. Vibrationally unrelaxed LIF spectrum of CS from the photolysis of CS_2 at 193 nm, measured with a frequency-doubled flashlamp-pumped dye laser.

laser intensity, this spectrum is taken under conditions similar to those used in Refs. 12 and 13. As is shown in Fig. 5 there is a significant amount of LIF from higher vibrational levels of the $X^{1}\Sigma^{+}$ following the photolysis of CS₂. The spectrum shows the presence of many vibrational bands originating from high vibrational levels of the ground state of CS. The assignment of the *R* branch bandheads are in agreement with those of Ref. 20. Although unresolved, the general shape of the spectrum shows that the CS is vibrationally hot. At lower pressures the spectrum is also rotationally excited.

The spectrum in Fig. 5 was taken with a pressure of 3 mTorr CS₂ in the cell and a delay of $2\mu s$ between the excimer and dye lasers. Under these conditions there should be no reaction or vibrational quenching. This indicates that there is a significant amount of nascent CS in vibrational levels above v'' = 5.

In order to obtain a better estimate of the nascent CS vibrational energy distribution, we used a Nd-YAG pumped dye laser which has a narrower bandwidth and a smaller pulse length, and rotationally cooled the nascent CS quantum state distribution by mixing argon with the CS_2 . Spectra were obtained throughout the 285-310 nm region. Figure 6(a) shows the observed LIF spectrum in the 287–293 nm region, where elements of the $\Delta v = -2$ and -3 sequences are excited. In this region there is at least one observable band originating in each ground state level from v'' = 5 to 12. This spectrum was normalized for excimer and doubled dye laser output. The spectral band intensities were converted into a measured vibrational level distribution after correction for the fluorescence filter transmission and Franck-Condon factors. A computer simulated spectrum of the above experimental result is shown in Fig. 6(b), and this reproduces the obtained LIF spectrum very accurately. From the constants used in this model, an even more accurate vibrational distribution can be obtained. This distribution is shown in Fig. 7. Our measurements for v'' = 5 are matched to those of Refs. 12 and 13 at v'' = 5, and the resulting global distribution is then normalized to unity.

If the average rotational energy for the nascent CS were small, the information from accurate LIF vibrational distributions (Fig. 7) and TOF spectra (Fig. 4) would be sufficient to determine the $S({}^{3}P)/S({}^{1}D)$ ratio. Butler *et al.*¹² measure a bimodal rotational distribution characterized by a Boltz-



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FIG. 6. (a) Rotationally relaxed LIF spectrum of CS. The spectrum was measured using a Nd-YAG pumped dye laser. (b) Computer modeled spectrum of LIF spectrum of CS shown in (a).

mann temperature of about 950 K (615 cm^{-1} or 1.9 kcal/ mol), and a substantially higher temperature distribution which dominates for state populations above J = 30. Yang *et* $al.^{13}$ indicate that the CS fragments have an average rotational energy of 3.5 kcal/mol (1200 cm^{-1}). For CS in vibrational levels higher than 5, we find that the average amount of rotational energy is of the order of 2000 cm⁻¹ (6 kcal/mol), as determined by fitting the general appearance of the spectrum to a computer modeled spectrum. This method may not be especially sensitive to the low temperature part of the bimodal distribution as measured in Ref. 12. The bimodal nature of the rotational distribution may reflect the nature of different dissociative surfaces leading to the production of $S(^{3}P)$ and $S(^{1}D)$.

A related problem is the question of whether the rotational cooling experienced by the nascent CS fragments at higher pressures resulted in significant vibrational scrambling or pooling. Fig. 5, which is taken under similar conditions as those in Refs. 12 and 13, shows that even under quasi-collision free conditions there is still population in vibrational levels above v'' = 5. Other spectra, not shown, measured with the Nd-YAG pumped dye laser, show the clear presence of these vibrational levels under totally collision-free conditions, in about the same ratios. The rotational cooling allows a better assignment of the population in each vibrational state. As a general rule, the rotational cooling process occurs on a much faster time scale than vibrational quenching or up-pumping.

C. S(3P)/S(1D) ratio

For the purposes of obtaining a $S(^{3}P)$ to $S(^{1}D)$ ratio we will first assume that the average amount of rotational ener-



FIG. 7. Vibrational distribution of nascent CS measured from LIF spectra of CS.

gy in all vibrational levels of CS is small. With this condition we obtain.

$$E_{\rm trans} = h\nu - D_0 - E_{\rm el} - E_{\rm vib} , \qquad (3)$$

where hv is the energy of a 193 nm photon, D_0 the CS₂ dissociation energy, $E_{\rm el}$ the electronic energy of the S atom, and $E_{\rm vib}$ the vibrational energy in the CS radical. Referring to Fig. 4, and as noted by Yang et al.,¹³ the part of the translational energy distribution above 18.6 kcal/mol can only be associated with the production of $S({}^{3}P)$ atoms. By the same token, the part of the vibrational distribution with v'' > 5 can also only be associated with the production of $S({}^{3}P)$ atoms. Since both curves are normalized to a total unit probability, the sum of these two contributions is a better lower limit on the $S(^{3}P)$ population of 38%. Figure 8 shows these two parts of the vibrational energy distribution mapped onto the translational energy distribution as open circles. The difference between the measured vibrational population of CS in v'' = 1-5 and that part of the distribution associated with high translational energy is the amount of CS produced in association with $S(^{1}D)$, where the contribution from rotation is neglected.

There is a small mismatch between the observed translational energy curve and the constructed translational energy distribution based on the synthesis of the high velocity part of the translational energy distribution and the vibrational distribution. This can be attributed to the neglected rotational energy distribution or distortions in the fragment distribution caused by sequential absorption of a second ArF laser photon by the CS product. This component would tend to increase the amount of $S({}^{3}P)$ associated with CS in vibrational states 4 and 5. However, such a correction could not amount to more than 10%. Thus, we confirm Yang et al.

measurement of ther $S(^{3}P)/S(^{1}D)$ branching ratio as being less than unity.

IV. DISCUSSION

Absorption spectroscopy maps the initially photoexcited state while TOF, LIF, and excited fragment emission spectroscopies measure the final state. The very short lived photoreaction complex is hard to probe, although recent developments in resonance Raman spectroscopy of dissociative states are very promising.23

The results of photofragment studies have been given in the previous section. The best spectroscopic evidence on the nature of the ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{1}B_{2}({}^{1}\Sigma_{u}^{+})$ transition of CS₂ comes from the work of Douglas and Zanon near the first measured band at 46 234 cm⁻¹,²³ and that of Hemley, Leopole, Roebber, and Vaida on the jet cooled absorption spectrum from 49 000 to 53 000 cm⁻¹.¹⁶ Since the 193 nm ArF laser illuminates the band at 51 750 cm^{-1} (red degraded), it is the latter study which correlates most directly with the ArF laser excited photofragment spectra.

There is a good overlap between the excimer laser, whose bandwidth FWHM is about 1 nm, and the bandhead of the CS₂ absorption band at 51 750 cm⁻¹. This particular band is the tenth member of a strong, regular progression measured by Hemley et al.¹⁶ However, Douglas and Zanon²⁴ have shown that there are at least three more weak members at longer wavelengths. In general the main progression involves the v_1 , symmetric stretch, on which are based shorter progressions and a v_2 bending mode. One refers ambiguously to a member of a progression rather than a detailed vibrational assignment because:

- (a) The symmetric stretch frequency of 392 cm⁻¹ is almost the same as the bending mode frequency of 426 cm^{-1} .
- (b) Although the system is regular above 49 000 cm⁻¹, it is impossible to assign the vibrational structure in detail below this energy. Douglas and Zanon ascribe this behavior to strong interactions between the almost degnerate modes v_1 and v_2 .



FIG. 8. Vibrational distributions of CS product associated with $S(^{3}P)$ and $S(^{1}D)$ fragments, mapped on the translational energy distribution.

(c) At higher energies there appears to be significant mixing between modes via chance resonances and anharmonic mixing.

There is good evidence from study of the vibrational hot bands that above 50 000 cm⁻¹ one excites the molecule to a quasi-linear configuration above the inversion barrier. As the excitation energy increases the intensity of the hot bands decreases and even in their maximum they make only a small contribution. Thus, most of the excitation is from the lowest vibrational level of the ground state, and one would not expect drastically different vibrational distributions in the nascent CS product even if the parent CS₂ were dramatically cooled in a seeded molecular expansion.

Following excitation at 193 nm the vibronically excited ${}^{1}B_{2}$ state is in a quasi-linear configuration, with at least 13 quanta in the combined ν_{1} and ν_{2} modes. Based on the short bending progressions, most of this excitation will be in the symmetric stretching mode, although at such high levels the normal mode picture may break down and there will be significant anharmonic mixing.

Table II shows the fraction of the available energy for a given channel that appears as vibrational and translational energy in the fragments. The results shown in this table suggest that the partitioning is the same in both channels. This comparison does not include an extensive study of the rotational energy in each state, but rather uses the estimates obtained in this work and Refs. 12 and 13 for a few vibrational levels.

Only a small amount of the available energy appears in rotation. At first glance this is surprising for a dissociation which involves a linear to bent excitation. However, as shown by the spectroscopy, the exited state is quasi-linear, with short bending progressions.

The remaining excess energy seems to be roughly partitioned between vibration in the CS fragment and relative translational energy. The spectroscopic evidence shows that the vibrational manifold of the excited $CS_2({}^{1}B_2)$ has up to 13 quanta in the symmetric stretch, with not much excitation of the bending modes. Unless there is a large amount of mixing between these modes before dissociation one would expect to find a considerable amount of vibrational energy in the CS fragment.

The predissociation lifetime has been measured by observing the broadening of the absorption lines as about 1 ps.²⁵ A lower limit of 0.6 ps was measured from the CS fragment anisotropy.¹³ The short predissociation lifetime of about 1 ps does not allow for total mixing between the bending and stretching modes, especially since the K' = 0 quan-

TABLE II. Fraction of available energy partitioned into translation and vibration of the CS fragment, for the photolysis of CS_2 in the following channels.

Channel	Fraction of energy in translation, f_t	Fraction of energy in vibration, f_v
$\overline{\mathrm{CS}_{2}\mathrm{CS}+\mathrm{S}(^{1}D)}$	0.47	0.53
$CS_2 CS + S(^3P)$	0.52	0.48

tum number of the initially excited state must be preserved. For a complete discussion of the experimental evidence showing that only K' = 0 is accessed, the reader is referred to Ref. 16.

The statistical expectation of energy partitioning between translation, vibration and rotation in the product channel is 3:2:2. In this case, we have seen that the transfer of energy to rotation is constrained by a Franck–Condon limitation of the excitation of the bending mode, which seems to translate into a dynamical constraint on the rotation. If we assume that none of the excess energy can be partitioned to rotation then the branching between translation and vibration will be 3:2. This branching is within the uncertainty of the experimental measurement.

Finally we come to the question of the electronic branching ratio. Conservation of spin angular momentum would require that the excited CS₂ undergo a singlet-triplet crossing from the ${}^{1}B_{2}$ state to produce S(${}^{3}P$). The relatively high mass of the S atoms in the molecule increase this probability. However, the mixing between the triplet and singlet surfaces must be small, and the crossover rate low. This can be deduced by noting that the singlet absorption is very strong, but triplet absorptions from the ground state are weak. If the states were strongly mixed the triplet would have borrowed strength from the singlet and its absorption would be relatively high. Moreover, statistically one would expect almost 14 times more triplet sulphur product than singlet, yet experimentally one measures only 0.5 times as much. Thus the singlet-triplet surface crossing must be a bottleneck in the dissociation dynamics.

V. CONCLUSIONS

Our experiments confirm the existence of populated vibrational levels up to and including v'' = 12. We measure a significantly higher proportion of slow CS fragments than were found in Ref. 13. The low branching ratio for the $S({}^{3}P)$ channel is confirmed. We are now conducting experiments using a higher-resolution dye laser system to exactly measure the rotational distributions of nascent CS. Some of these measurements will be made in cooled seeded beams, which will allow a direct inversion of the rotational distributions to impact parameters, and a construction of the potential energy surface.

ACKNOWLEDGMENTS

We are grateful for NASA grant #5071 which provided support for R. Lu and V. McCrary, grant #NAGW-446 which provided support for J. A. Russell, ONR contract #N00014-80-C-0305 which provided partial support for W. M. Jackson, and NSF grant #CHE 8219255 which partially supported J. B. Halpern.

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